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Fabrication and Characterization of PMMA based Composite Gas Sensor

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ABSTRACT

Gas detection instruments are increasingly needed for industrial health and safety, environmental monitoring and process control. To meet this demand, considerable research into new type of sensors is underway to enhance the performance of traditional devices. The polymer–ceramic composites have superior characteristics and play vital role in gas sensing applications. The gas sensors based on Carbon nano tube/polymer, ceramic and metal oxide composites such as epoxy, polyimide, PMMA/ $BaTiO_3$ and SnO_2 have also been developed. In the present study, a new set of composites were prepared by using zirconium titanate and PMMA. Characterisation of the synthesized composites was done by using PXRD and FTIR. The thick films of the composite were prepared by using a spin coating unit. The application of the thick film as gas sensor has been studied on exposure to gaseous vapours at atmospheric temperature. The gas sensing efficiency of the composite was analysed for different vapours. The results show that the thick film of the prepared composite can function as a very good gas sensors.

Keywords: Polymer composite, PMMA, Zirconium titanate (ZT), gas sensor.

1. INTRODUCTION

Composites are materials obtained by bonding two or more materials together. The characteristics of the resulting materials are not that of the components in isolation. Advanced composites of low weight can be substitutes for metallic parts. Application of polymer composites as engineering materials has become the state of the art. Polymer composites which fit into particular engineering applications can be designed by selecting the correct composition and choosing the appropriate manufacturing process[1]. Evaluation of composites for special engineering applications requires property investigation.

Piezoelectric ceramics have good detection and output characteristics and thus used as sensors. Pure piezoelectric ceramics are often too stiff and brittle. If piezoelectric ceramic particles are incorporated within a polymer matrix, it will result in composite sensors containing both piezoelectric and visco elastic properties. The polymers have become inheritable in sophisticated electronic measuring devices such as sensors. Both intrinsically conducting polymers and non-conducting polymers are used in sensor devices. Electrically conducting organic polymers are important in sensing devices[2-4]. Polymers used in sensor devices either participate in sensing mechanisms or immobilize the component responsible for sensing the analyte.

The emission of gaseous pollutants such as sulphur oxide, nitrogen oxide and toxic gases from related industries has become a serious environmental concern**.** Thus sensing devices need to be installed in such places. These devices should be cheap, reagentless and able to quantify the levels of gases in a rapid manner, at room temperature with low power consumption[5]. The room temperature gas sensing property is very attractive for many applications[6,7]. A novel fluorescent polymer PMMA-PM for optical sensing prepared using electrospinning technique has been reported[8]. A new multilayer integrated optical sensor (MIOS) for ammonia detection at room temperature using PMMA and PANI has also been reported[9]. PMMA-Polypyrrole composite films were prepared electrochemically and used as gas sensors by observing the change in the current when exposed to ammonia gas and the film gives a fast and reproducible response towards ammonia gas[10]. A nanofibrous sensor for ammonia gas fabricated by using polydiphenylamine (PDPA) with PMMA onto patterned interdigit electrode has been reported. The functional groups in PDPA and the high active surface area of the fibrous membrane combine together and thus enable the device to detect a lower concentration of ammonia with good reproducibility[11]. Composite of MWCNT and PMMA has been prepared for gaseous toluene detection[12].

The polymer composite developed through dissolution of styrene and polyaniline in PMMA is used as polymer gas sensor arrays for electronic nose[13]. Chemical sensors have been used in industrial processing, environmental monitoring and inflammable environments for human safety[14]. Colorimetric gas sensors[15], selective and low-cost colorimetric gas sensors have been reported[16]. Humidity sensing properties of PMMA were enhanced by doping with two alkali salts (KOH and K_2CO_3) has also been reported[17]. Pulsed high magnetic field sensor using PMMA has been reported[18]. A compact wireless gas sensor using a CNT and PMMA thin film resistor shows fast response and change in resistance from 102 to 103 due to surface modification[19]**.** In fact, analytical gas sensors offer a promising and inexpensive solution to problems related to hazardous gases in the environment. Amperometric sensors consisting of an electrochemical cell in a gas flow which respond to electrochemically active gases and vapours have been used to detect hazardous gases and vapours[20,21]. Most of the widely studied conducting polymers in gas sensing applications are polythiophene

and its derivatives[22,23] polypyrroles[24,25], polyaniline and their composites[22,26].

2. EXPERIMENTAL SECTION

Materials

The monomer MMA, zirconium titanate, benzoyl peroxide, chloroform and petroleum ether were obtained from SD Fine Chemicals Limited, Mumbai, India.

Preparation of PMMA

The purified monomer (MMA) (10ml) was taken in a polymerization tube and 50mg of benzoyl peroxide which acts as a catalyst was added to accelerate polymerization, in the polymerization reaction. The polymerization tube was then kept in a water bath at 60-70^{o}C with periodical shaking. A hard viscous polymer was obtained after 90 minutes of heat treatment. The polymerized mass was dissolved in chloroform and then transferred into a beaker. The viscous polymer solution was precipitated by the addition of petroleum ether. The precipitated polymer was then filtered and oven dried at 60^{o}C. The polymer formed was found to be syndiotactic[27].

Preparation of PMZT 1 and PMZT 2

Polymer composite sample 1 (PMZT 1) was prepared as follows: 2g of PMMA was dissolved in chloroform. 2g of zirconium titanate was then added and made into a paste in an agate mortar and was subjected to heat at 110°C for 6 hours in a Muffle furnace and made into a powde Polymer composite sample 2 (PMZT 2) was prepared by using 1.5g of PMMA in chloroform and 0.5g of zirconium titanate , following the above steps.

Thick film of the prepared composite over glass substrates was formed by using a spin coating unit (SCU 2005) at 9000rpm.

Gas sensor based on PMZT composite

PMMA based composites (PMZT) were uniformly coated onto a glass strip to form (PMZT) composite gas sensor. Two parallel copper wires were fitted onto the corners of the glass strips. These wires act as electrodes to detect the presence of gas as well as its concentration. For this study, acetone and ethanol gas was used and the electrical resistance of (PMZT) composites over acetone and ethanol vapours was determined using MECO 603 digital multimeter.

The change in the electrical resistance of the (PMZT) composites when exposed to acetone and ethanol gas was determined. Vapours of volatile liquids were generated using a closed glass chamber. The electrical resistance on composite was recorded till it reaches its equilibrium. A given volume of liquid was injected into the chamber, which had a known volume.

3. RESULTS AND DISCUSSION

Characterization

In order to understand the properties of composite material, it is essential to know about the details of its structure. Diffraction techniques were adapted to characterize the synthesized composites. The X-ray diffraction pattern (XRD) technique was used for characterization.

The PXRD of PMMA, zirconium titanate, PMZT 1 and PMZT 2 were recorded using X'PERT PRO diffractometer.

XRD

The XRD peaks of the PMMA, zirconium titanate and the composites were compared in the figure 1. The XRD analysis of PMZT 1 and PMZT 2 showed a similar pattern. While analyzing the composite peaks, the intensities of the precursor peaks were not reflected. At the same time, the positions of few peaks in the composites have been shifted compared to zirconium titanate peaks.

Responsiveness of composite

When the electrical resistance of the composite approached its equilibrium value, the composite sensor was removed from the closed vessel to record the change in electrical resistance. No change in electrical resistance was recorded in air after the composites reaction inside the closed vessel.

The responsiveness, S, of the composites to various solvents can be determined from the equation,

$$S = (R_t - R_o) / R_o$$

Where Ro is the initial resistance value, and R_t is the maximum steady state response value. The measurements were made by exposing the sensor in acetone gas every 10 seconds. It can be seen from the figures 2 and 3, that the response of the sensor is fast and it returns to the initial level immediately after it is removed from the gas. Measurements were repeated for ethanol and acetone gases, and the responsiveness of the sensor was calculated for the same (Table 1).

3.1. Impact of exposure

The responses of the sensors (Figures 2 and 3) were observed for the two different gases by measuring the change in resistance due to exposure of gases. Acetone and ethanol were used. It was observed from the measurements that each solvent had its own impact on the variation of resistance, which is good for the detection and identification of gases. It was observed that the variation of resistance for PMMA/ZT composite was predominant in the case of ethanol.

Table. 1. Sensor response of PMZT composite films

		R_o (ohms)	**R_t (ohms)**	**$(R_t - R_o)/ R_o$**
Ethanol	PMZT 1	0.1	12.92	128.2
	PMZT 2	0.2	13.25	65.25
Acetone	PMZT 1	0.35	11.68	32.372
	PMZT 2	0.45	12.66	27.13

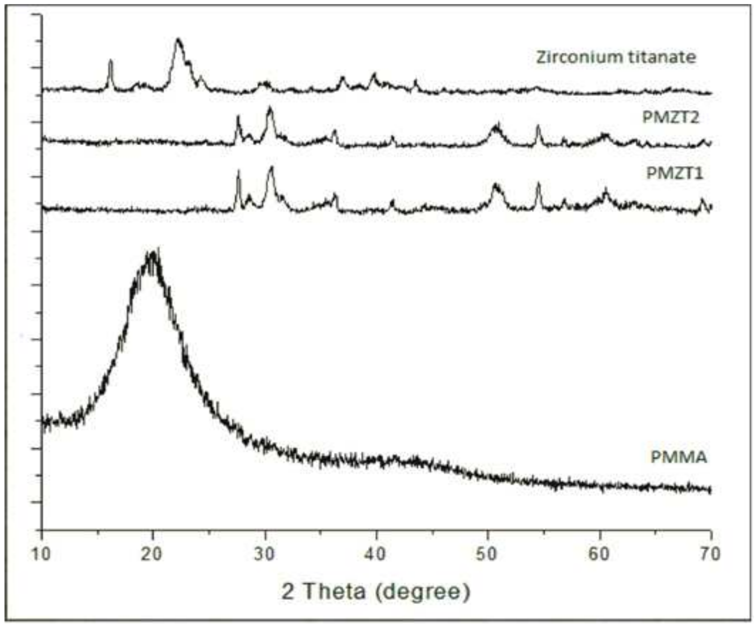

Figure.1. XRD patterns of PMMA, PMZT 1, PMZT 2 and ZT

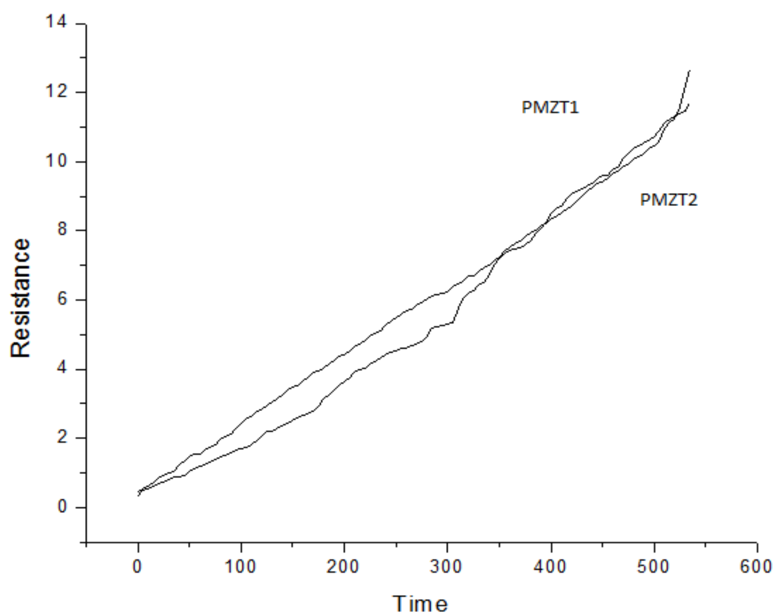

Figure. 2. Sensor response in acetone vapours

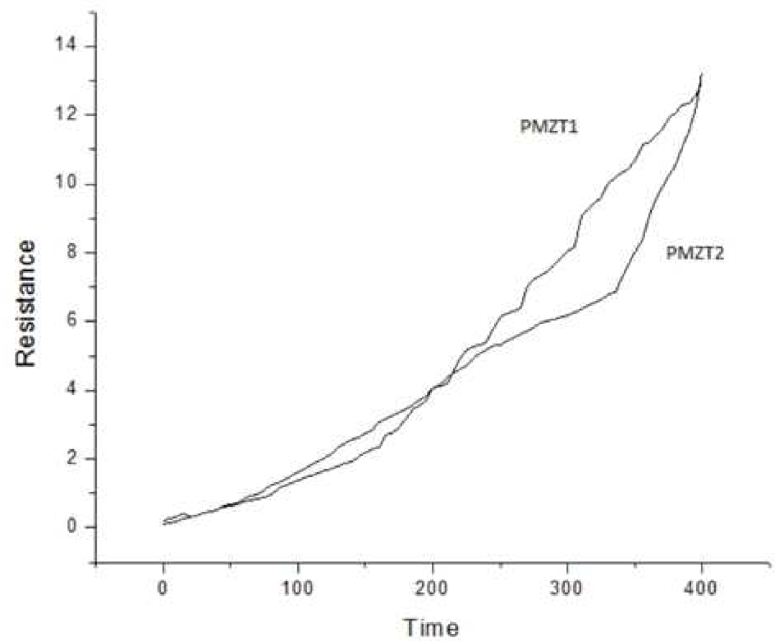

Figure. 3.Sensor response in ethanol vapours

4. CONCLUSION

PMMA based gas sensor has been developed and the experimental results are evaluated. The sensitivity of the gas detector is reflected by the change in resistance of the composite film due to exposure to gases. The responses of the sensor for gases namely acetone and ethanol was recorded. The resistance response model for the gas at 100% concentration were determined. The electric resistance of the polymer composite extremely increased in acetone and ethanol vapours and returned immediately to initial resistance when it was transferred to dry air. The results have shown that PMMA based composites have potential application for detecting vapours.

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